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Analytical Expression of Nonlinear Partial Differential Equations in Mediated Electrochemical Induction of Chemical Reaction

*V. Ananthaswamy[1], C. Thangapandi[2], J. Joy Brieghti[3], M. Rasi[4], L. Rajendran[5]

[1,2,4] Department of Mathematics, The Madura College (Autonomous), Maduri, Tamil Nadu, India

[3] M. Phil., Mathematics, The Madura College (Autonomous), Maduri, Tamil Nadu, India

[5] Department of Mathematics, Sethu Institute of Technology, Madurai, Tamil Nadu, India

[1] ananthu9777@rediffmail.com*; [2] ctmaths@gmail.com; [3] joybrieghti123@gmail.com; [4] rasildc@gmail.com;

[5] raj_sms@rediffmail.com

Abstract

In this research article, we discuss the non-steady state concentration of mediator of electrochemical induction in chemical reactions. This paper presents an approximate analytical method (Homotopy and new approach to the Homotopy perturbation method) to solve the nonlinear differential equations. A simple and closed form of an analytical expression of non-steady state concentrations and effectiveness factors of current is pertaining for all values of the dimensionless parameters. The numerical simulation of the problem is also reported using the Matlab/Scilab software program. The analytical results are compared with numerical results and are found to be good in the agreement. The obtained results are valid for the whole solution domain.

Keywords

Mediated Concentration; Current; Mathematical Modeling; Initial-boundary Value Problem; Numerical Simulation; Laplace-homotopy Perturbation Method

Introduction

There are many methods for analysis electro-chemical reactions. One of the methods is a mediated electro analysis by use of electrochemical induction, that is used in this paper. The redox compound mediated and electro catalyzed methods process is called mediated electro analysis [Mèdebille et.al (1991)]. Mediated electrochemical induction is indirect and also more systematically exploited [Anderiex et. Al (1980)]. The main idea of this problem is electron transfer in reactant to product with mediators [Mèdebille et.al (1997)]. In addition redox titration between the substrate and the result of the experiment. The electrochemical potential of redox active compounds can be determined in solution by applying a redox titration.The absorption spectrum of the investigated compound is observed [Mèdebille et.al (1991)]. The potential of the solution is changed by adding a reducing or oxidizing agent. If the potential in the solution is negative (positive) enough to reduce (oxidization) the investigated compound, the optical spectrum will change until the reduction (oxidation) is complete [Andrieux et.al (1991)]. In the mediated electrochemical process is faster than in, direct electrochemical induction [2]. In this paper the author analysied electrochemical induction of the nucleophillic substitution of perfluorohexyl iodide by 2-methyl-5-nitroimidazolate ions (Nu^-) in acetonitrile mediated by the 4-nitropyridine-N-oxide anion radical, and give an experimental by use of above described method [Mèdebille et.al (1991)]. The indirect (mediated) electrochemistry should be more systematically exploited. Areactant is generated electrochemically and its homogeneous reaction with the substrate can be monitored by the ensuing variation of the current . The reactions of single electrons as well as of electron pair donors or acceptors can be followed by this method [Bard et.al (2001)]. This in

situgeneration allows the investigation of very reactive species, the only limit being that they should react with the substrate faster than they react with any other molecule present in the solution [Savant et.al (1997)]. Then mathematical modeling eqns (1-5), are converted in theose eqns. In the mediated electrochemical process these reactions are faster than electron transfer to (or) from B , the overall kinetics will depend on a competition between reaction and first order deactivation reaction [Mèdebille et.al (1991)]. The purpose of this paper is to derive the analytical expressions for mediated concentrations for substrate and the dimensionless current using the new approach to Homotopy perturbation method.

Mathematical Formulations of the Problem

The mathematical model for estimating the electrochemical reactions was set forth by Saveants (1997) and further developed by Mèdebille et. al (1991). This problem based on electrochemical reaction with the use of redox titration. The substrate reactant converted to products using redox couple P/Q [Mèdebille et.al (1991)].

$$P \pm e^{-} \Leftrightarrow Q \tag{1}$$

$$Q + A \xrightarrow{k_1} B + P \tag{2}$$

$$B \xrightarrow{k_2} C \tag{3}$$

$$C + P \xrightarrow{k_3} D + Q \tag{4}$$

$$A \rightarrow D \tag{5}$$

The above kinetics reaction eqns.(1)-(5) are formed by the following set of nonlinear partial differential equations,with initial and boundary conditions:

$$\frac{\partial p}{\partial \tau} = \frac{\partial^2 p}{\partial y^2} + \lambda_1 aq - \lambda_3 cp \tag{6}$$

$$\frac{\partial q}{\partial \tau} = \frac{\partial^2 q}{\partial y^2} - \lambda_1 aq + \lambda_3 cp \tag{7}$$

$$\frac{\partial a}{\partial \tau} = \frac{\partial^2 a}{\partial y^2} - \lambda_1 aq \tag{8}$$

where

$$\lambda_2 b = \lambda_3 cp,\ \lambda_1 aq = (\lambda_2 + \lambda_4) b \tag{9}$$

The initial and boundary conditions are,

$$\tau = 0, y \geq 0 \ and \ y = \infty \quad \tau \geq 0 : p = 1, q = 0, a = \gamma \tag{10}$$

$$y = 0, \tau \geq 0 : \frac{\partial p}{\partial y} + \frac{\partial q}{\partial y} = 0,\ p = q * e^{-\xi}, \frac{\partial a}{\partial y} = 0 \tag{11}$$

where

$$\tau = (FV / RT)t,\ \ \xi = -(F / RT)(E - E_{PQ}^{0}),$$
$$y = x(FV / RT)^{\frac{1}{2}} \tag{12}$$

$$\lambda_1 = \frac{RT}{F}\frac{k_1 c_p^0}{\upsilon},\ \lambda_2 = \frac{RT}{F}\frac{k_2 c_p^0}{\upsilon}, \lambda_3 = \frac{RT}{F}\frac{k_3 c_p^0}{\upsilon},$$
$$\lambda_4 = \frac{RT}{F}\frac{k_4 c_p^0}{\upsilon}, \gamma = \frac{c_A^0}{c_p^0}, \sigma = \frac{\lambda_4}{\lambda_2 + \lambda_4} = \frac{k_4}{k_2 + k_4} \quad , \tag{13}$$

where a, p, q are the concentrations of the corresponding substrates, that's been normalized, with respect to the concentration of substrate of the bulk solution c_p^0 and k_1, k_2, k_3, k_4 are rate constants of the corresponding reactions.

We introduce the $a^* = \sigma a$ into the precedingeqns, we obtain with the initial and boundary conditions.

$$\frac{\partial q}{\partial \tau} = \frac{\partial^2 q}{\partial^2 y} - \lambda_1 a^* q \tag{14}$$

$$\frac{\partial a^*}{\partial \tau} = \frac{\partial^2 a^*}{\partial^2 y} - \lambda_1 a^* q \tag{15}$$

$$\tau = 0,\ y \geq 0, y = \infty,\ \tau \geq 0 :\ q = 0,\ a^* = \gamma^* = \sigma\gamma \tag{16}$$

$$y = 0,\ \tau \geq 0 :\ q\frac{1}{1+e^{\xi}},\ \frac{\partial a}{\partial y} = 0 \tag{17}$$

The cyclic voltametric wave is given by,

$$\frac{I_p}{I^0{}_p} = \frac{1}{0.446}\left(\frac{\partial q}{\partial y}\right)_{y=0} \tag{18}$$

Analytical Solutions of the Concentrations and Current Using the Homotopy and New Approach to Homotopy Perturbation Method

Recently, many authors have applied the Homotopy perturbation method (HPM) to solve the non-linear problem in physics and engineering sciences [He (1999 & 2003), Ariel (2010), Ananthaswamy et.al (2013) and]. This method is also used to solve some of the non-linear problem in physical sciences [Shanthi et.al (2013 & 2014)]. This method is a combination of Homotopy in topology and classic perturbation techniques. Ji-Huan He used to solve the lighthill equation, the duffing equation and the blasius equation (1999 and 2003)]. The HPM is unique in its applicability, accuracy and efficiency. The HPM uses the imbedding parameter p as a small parameter, and only a few iterations are needed to search for an asymptotic solution. By solving the eqns. (14) and (15) the mediated concentrations *q(y,t)* and *a(y,t)* can be obtained by the following eqns.

$$q(y,t) = \frac{e^{-t\sqrt{b}}\left[\begin{array}{l} erf\left(\frac{2t\sqrt{b}\_y}{2\sqrt{t}}\right)+1 \\ +e^{2y\sqrt{b}}erfc\left(\frac{2t\sqrt{b}+y}{2\sqrt{t}}\right)\end{array}\right]}{2(e^{-\xi}+1)} \tag{19}$$

$$a(y,t)=\sigma\gamma-\frac{\lambda_1\sigma\gamma}{2\left(1+e^{-\xi}\right)}\left\{\begin{array}{l}\left(t+\frac{y^2}{2}\right)erfc\left(\frac{y}{2\sqrt{t}}\right)\\ +y\left(\begin{array}{l}y\,erf\,\frac{y}{2\sqrt{t}}\\ +2\frac{\sqrt{t}\,e^{\left(\frac{-y^2}{4t}\right)}}{\sqrt{\Pi}}\\ -y\end{array}\right)\\ -\frac{\sqrt{t}\,ye^{\left(\frac{-y^2}{4t}\right)}}{\sqrt{\Pi}}\end{array}\right\} \tag{20}$$

We use the value of mediated concentration q in the eqn.(20), then we get the normalized current inthe eqn.(21).

$$\begin{aligned}\psi&=\left(\frac{\partial q}{\partial y}\right)_{y=0}\\ &=\frac{1}{4}\left(\frac{-\sqrt{b}\,erf\,(2\sqrt{bt})+4\sqrt{b}-2\sqrt{b}\,erfc(2\sqrt{b}+t)}{\sqrt{t}(e^{-\xi}+1)}\right)\end{aligned} \tag{21}$$

Numerical Solution

The nonlinear differential eqns. (14) - (17) are also solved using numerical methods. The function pdex4 in Matlab/Scilab software function which is solving the partial differential equation. Its numerical solution is compared with Homotopy perturbation method and it gives satisfactory results.

Results and Discussion

Figure 1 and 2 show the mediator concentration $q(y,t)$ versus dimensionless distance y. From Fig. 1 (a), it is clear that when the the excess parameter γ increases, the corresponding mediator concentration $q(y,t)$ decreases in some fixed values of the other dimensionless parameters σ, λ_1, ξ and t. From Fig. 1(b), we notice that when the ratio of rate constant σ increases, the corresponding mediator concentration $q(y,t)$ also increases in some fixed values of the other dimensionless parameters. From Fig. 2(a), we infer that when the spherical diffusion parameter ξ increases, there is no change in the mediator concentration $q(y,t)$ in some fixed values of the other dimensionless parameters. From Fig 2(b) it is clear that when dimensionless time t increases, the corresponding mediator concentration $q(y,t)$ also increases in some fixed values of the other dimensionless parameters.From Fig 2(c) is observe that when the rate constant λ_1 decreases. the mediated concentration $q(y,t)$ decreases in some fixed values of the other dimensionless parameters.

Figure 3 and 4 show the mediator concentration $a(y,t)$ versus dimensionless distance y, for various dimensionless factors $\sigma, \gamma, \lambda_1, \xi, t$. From Fig. 3 (a), it is clear that when the the dimensionless time t decreases the corresponding mediator concentration $a(y,t)$ increases in some fixed values of the other dimensionless parameters. From Fig. 1(b), we notice that when the excess parameter γ increases, the corresponding mediator concentration $a(y,t)$ increases in some fixed values of the other dimensionless parameters. From Fig. 4(a), its clear that when the rate parameter λ_1 decreases, the corresponding mediator concentration $a(y,t)$ increases in some fixed values of the other dimensionless parameters. From Fig 4(b) it is notice that when the excess parameter γ increases, the corresponding mediator concentration $a(y,t)$ increases in some fixed values of the other dimensionless parameters. From Fig 4(c) when the spherical diffusion parameter ξ increases, the corresponding mediator concentration

$a(y,t)$ increases in some fixed values of the other dimensionless parameters. Figure 5 and 6 indicate the three dimensional diagram for $q(y,t)$ and $a(y,t)$ with respect to λ_1 and σ and for various values of the other dimensionless parameters. The normalized current ψ versus the dimensionless excess parameter γ^* are presented in Figures.7(a)-(d) in some fixed values $\lambda_1 = 0.45, \xi = 0.1, \sigma = 3$. Figure 7(a) and (c) it is clear that when ratio of rare constant , spherical diffusion parameter and dimensionless time,corresponding the normalized current decreases for various values of dimensionless parameters. From Fig 7(d) it is clear that the when rate parameter λ_1 increases the corresponding normalized current increases for different values of dimensionless parameters. Table 1 represents the error table for the analytical results (eqns. (19) and (20)) and numerical simulation for the dimensionless parameters λ_1.

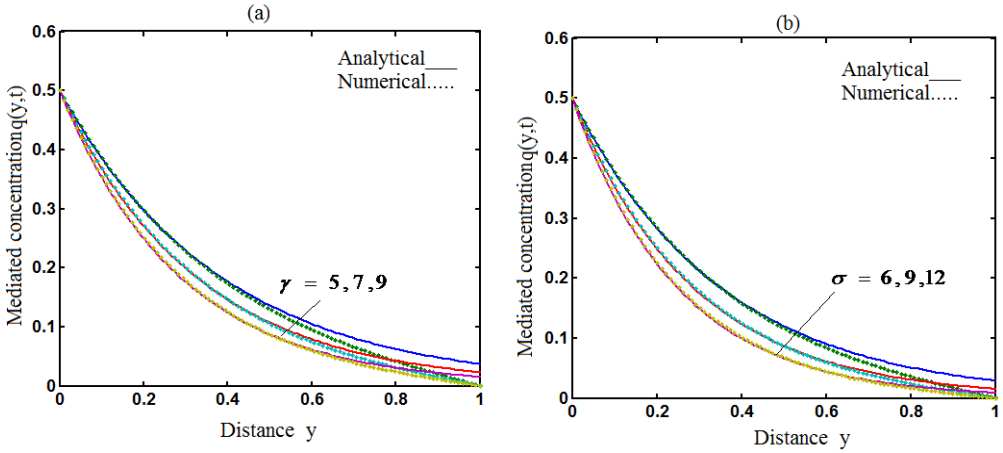


FIGURE 1. PLOT OF THE MEDIATED CONCENTRATION $q(y,t)$ VERSUS DIMENSIONLESS DISTANCE Y IN SOME FIXED VALUES OF THE DIMENSIONLESS PARAMETERS $\lambda_1, \xi, t, \gamma$, and σ WHEN (a) $\lambda_1 = 0.45$, $\xi = 0.001$, $t = 1$, $\sigma = 3$ AND $\gamma = 5,7,9$ (b) $\lambda_1 = 0.45$, $\xi = 0.001$, $t = 1, \gamma = 4$ AND $\sigma = 6,9,12$ USING THE EQN. (19).

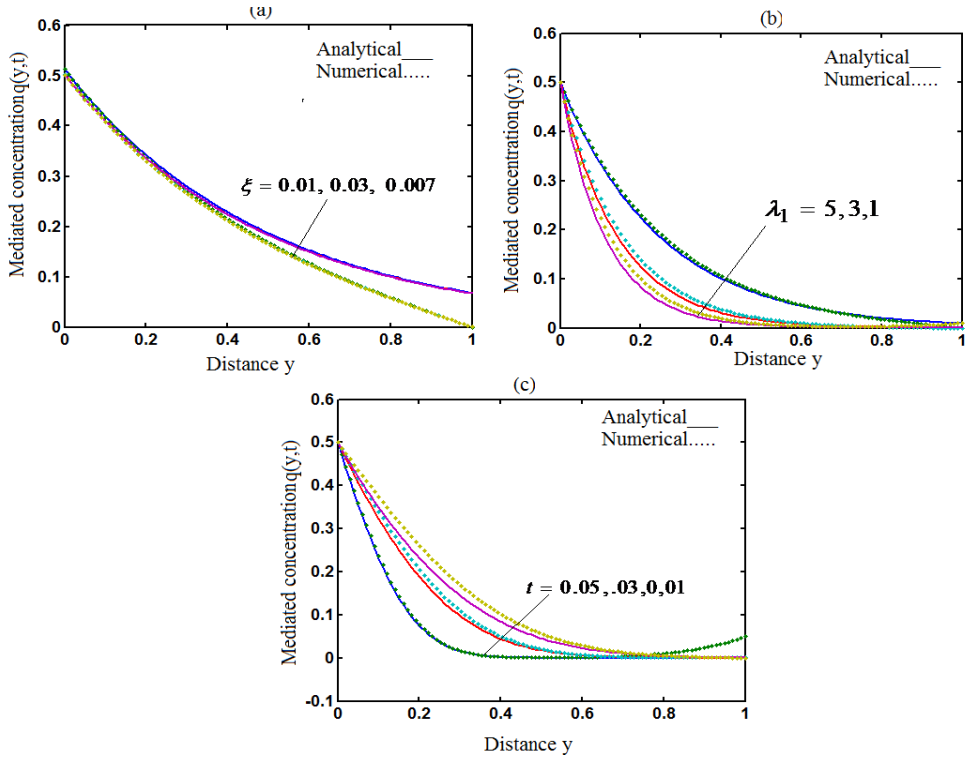


FIGURE 2. PLOT OF THE MEDIATED CONCENTRATION $q(y,t)$ VERSUS DISTANCE Y IN SOME FIXED VALUES OF THE DIMENSIONLESS PARAMETER $\lambda_1, \xi, t, \gamma$, and σ, WHEN (a) $\lambda_1 = 0.45$, $t = 1$, $\gamma = 4, \sigma = 3$ and $\xi = 0.01$, 0.05, 0.007 (b) $\xi = 0.001$, $t = 1$, $\gamma = 4, \sigma = 3$ AND $\lambda_1 = 5,3,1$ (c) $\lambda_1 = 0.45$, $\xi = 0.001$, $\gamma = 4, \sigma = 3$ and $t = 0.05, 0.01, 0.007$ USING THE EQN.(19).

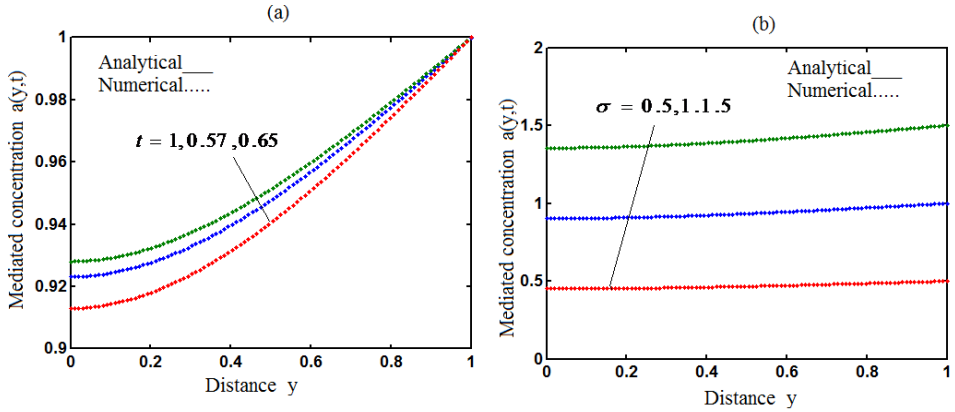
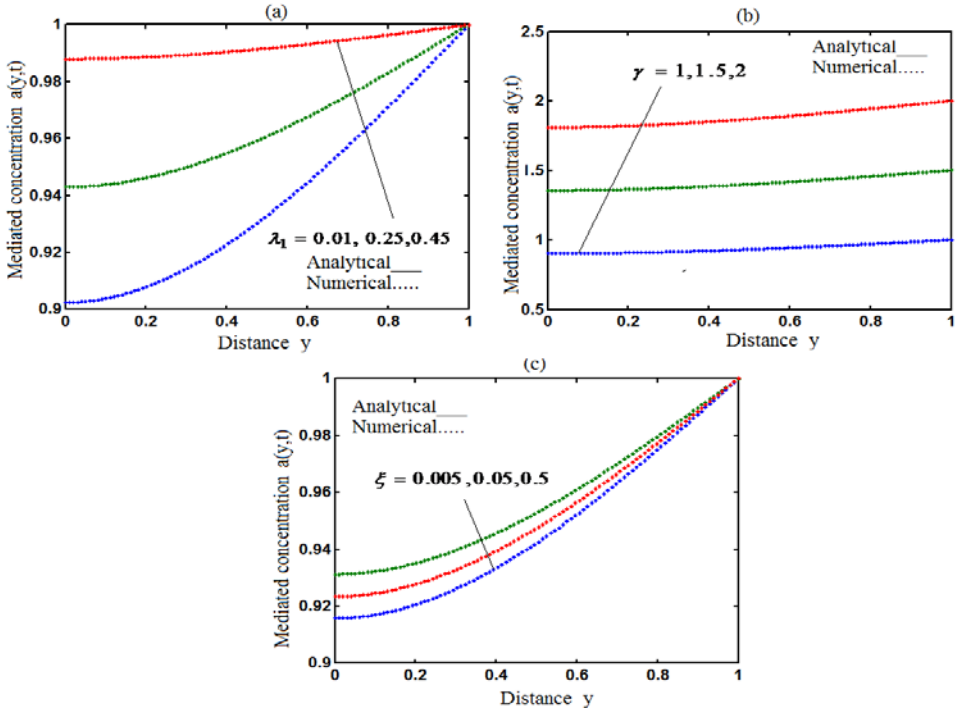


FIGURE 3. PLOT OF THE MEDIATED CONCENTRATION $a(y,t)$ VERSUS DIMENSIONLESS DISTANCE Y IN SOME FIXED VALUES OF THE DIMENSIONLESS PARAMETERS $\lambda_1, \xi, t, \gamma$, and σ WHEN (a) $\lambda_1 = 0.45$, $\xi = 1$, $\gamma = 1, \sigma = 1$ AND $t = 0.57, 0.65, 1$ (b) $\lambda_1 = 0.45$, $\xi = 1$, $t = 1, \gamma = 1$ AND $\sigma = 0.5, 1, 1.5$ USING THE EQN. (20).



FIGRE 4. PLOT OF THE MEDIATED CONCENTRATION $a(y,t)$ VERSUS DIMENSIONLESS DISTANCE Y IN SOME FIXED VALUES OF THE DIMENSIONLESS PARAMETERS $\lambda_1, \xi, t, \gamma$, and σ WHEN (a) $t = 1$, $\xi = 1$, $\gamma = 1, \sigma = 1$ AND $\lambda_1 = 0.01, 0.25, 0.45$
(b) $\lambda_1 = 0.45$, $\xi = 1$, $t = 1, \sigma = 1$ AND $\gamma = 1, 1.5, 2$
(c) $\lambda_1 = 0.45$, $t = 1, \sigma = 1$ and $\xi = 0.005, 0.05, 0.5$ USING THE EQN. (20).

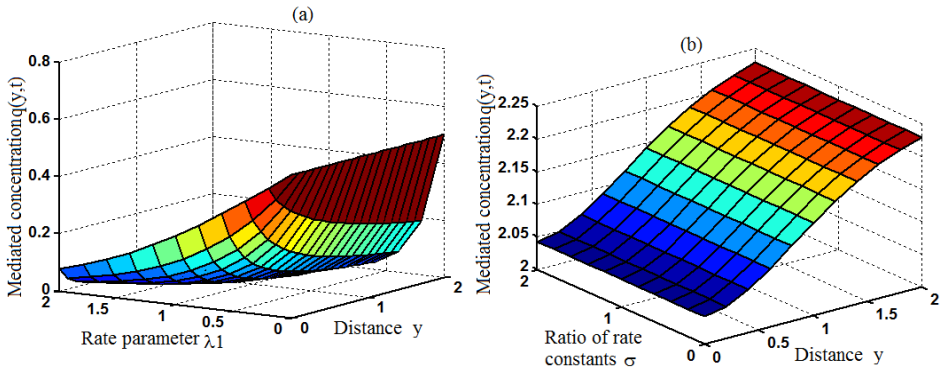


FIGURE 5. THE MEDIATED CONCENTRATION OF $q(y,t)$ IS PLOTTED. THE GRAPH WAS CONSTRUCTED USING EQN. (19) FOR THE DIMENSIONLESS PARAMETERS λ_1 and σ.

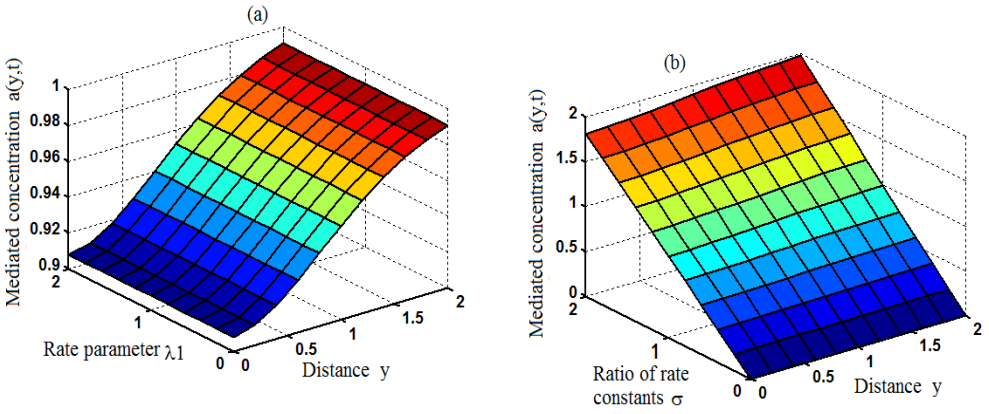


FIGURE 6. THE MEDIATED CONCENTRATION OF $a(y,t)$ IS PLOTTED. THE GRAPH WAS CONSTRUCTED USING EQN. (20) FOR THE DIMENSIONLESS PARAMETERS λ_1 and σ.

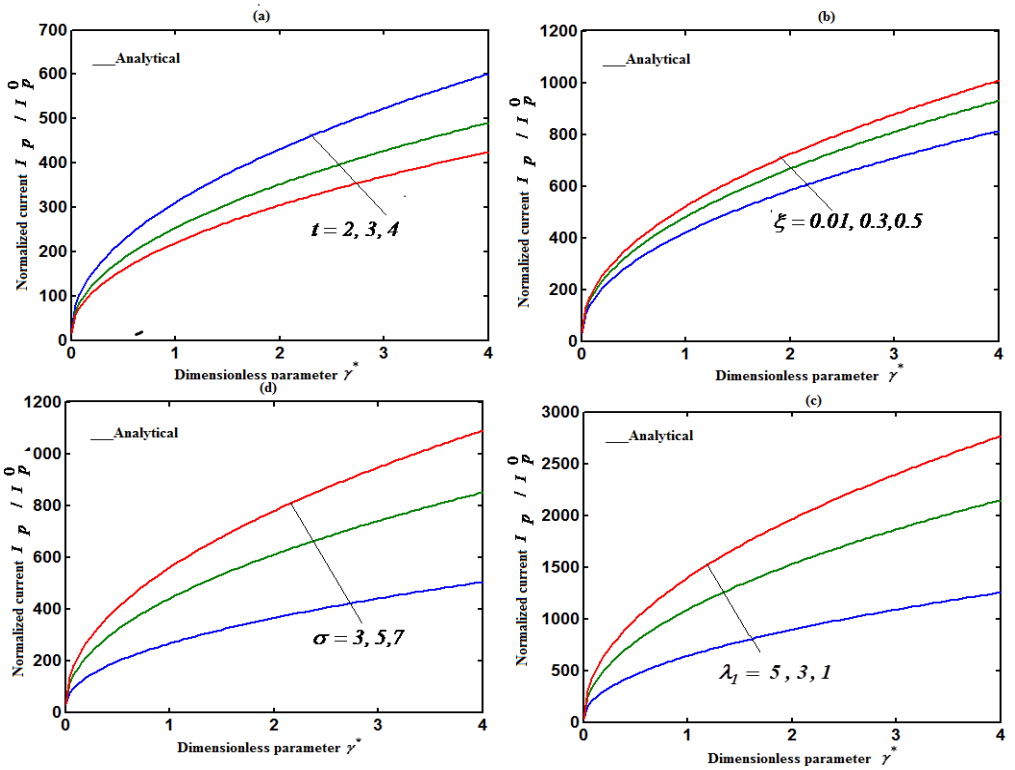


FIGURE 7. PLOT OF THE NORMALIZED CURRENT ψ VERSUS γ IN SOME FIXED VALUES OF THE DIMENSIONLESS PARAMETERS λ_1, ξ, t and σ WHEN (a) $\lambda_1 = 0.45$, $\xi = 0.001$, $\sigma = 4$ and $t = 2, 3, 4$ (b) $\lambda_1 = 0.45$, $t = 1$, $\sigma = 4$ and $\xi = 0.01, 0.03, 0.05$, (c) $\lambda_1 = 0.45$, $t = 1$, $\xi = 0.001$ and $\sigma = 3, 5, 7$ (d) $\xi = 0.001$, $t = 1$, $\sigma = 4$ and $\lambda_1 = 1, 3, 5$ USING THE EQN.(21).

TABLE: 1A COMPARISION OF OUR ANALYTICAL RESULT OF MEDIATOR CONCENTRATION $q(y,t)$ VERASUS DIMENSIONLESS DISTANCE Y WITH THE NUMERICAL SIMULATION FOR VARIOUS VALUES OF λ_1 THE USING EQN.(19) WHEN $\xi = 0.001$, $t = 1$, $\gamma = 4$, *and* $\sigma = 3$

y	$\lambda_1 = 1$			$\lambda_1 = 3$			$\lambda_1 = 5$		
	Analytical	Numerical	(%) of deviation	Analytical	Numericl	(%) of deviation	Analytical	Numerical	(%) of deviation
0	0.50025	0.5002	.019	0.50025	0.5002	.019	0.50025	0.5002	.019
00.2	0.23	0.23	0	0.151	0.123	0.03	.1	0.1	0
0.4	0.101	0.108	2.84	0.045	0.00364.	2.5	0.02	0.02	0
0.6	0.045	0.047	4.25	0.01	0.01	0	0.0047	0.0004	1.75
0.8	0.02	0.02	0	0.003	0.002	.5	0.001	0.00003	2.3
1	0.02	0.02	0	0.002	0.002	0	0.0002	0.000007	3.52
	Average % of deviation		1.15	Average % of deviation		0.51	Average % of deviation		1.26

TABLE: 1B COMPARISION OF OUR ANALYTICAL RESULT OF MEDIATOR CONCENTRATION $a(y,t)$ VERASUS DIMENSIONLESS DISTANCE Y WITH THE NUMERICAL SIMULATION FOR VARIOUS VALUES OF λ_1 THE USING EQN.(20) WHEN $\xi = 1$, $t = 1$, $\gamma = 1$, and $\sigma = 1$

y	$\lambda_1 = 0.01$			$\lambda_1 = 0.25$			$\lambda_1 = 0.45$		
	Analytical	Numerical	(%) of deviation	Analytical	Numericl	(%) of deviation	Analytical	Numerical	(%) of deviation
0	0.9024	0.9024	0	0.943	0.943	0	0.988	0.988	0
00.2	0.9075	0.9075	0	0.946	0.946	0	0.9905	0.9905	0
0.4	0.9222	0.9222	0	0.9551	0.9551	0	0.9931	0.9931	0
0.6	0.9441	0.9441	0	0.9441	0.9441	0	0.9933	0.9933	0
0.8	0.9722	0.9722	0	0.9681	0.9681	0	0.9966	0.9966	0
1	1	1	0	1	1	0	1	1	0
	Average % of deviation		0	Average % of deviation		0	Average % of deviation		0

Conclusion

In this paper a Homotpy and new approach to Homotopy perturbation method (HPM) is successfully applied for solving nonlinear partial differential equation. Approximate analytical expressions of the mediated concentrations of substrate in the electrochemical reaction using in induction method for all values of the dimensionless parameters is obtained using the HPM. The results are compared with the numerical simulation and it gives satisfactory agreement. This method can be easily extended to solve the other strongly nonlinear initial and boundary value problems in physical, chemical and biological sciences.

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Appendix A:

Basic Concept of the Homotopy Perturbation Method [He (1999 and 2003)]

To explain this method, let us consider the following function:

$$D_o(u) - f(r) = 0, \quad r \in \Omega \tag{A.1}$$

with the boundary conditions of

$$B_o(u, \frac{\partial u}{\partial n}) = 0, \quad r \in \Gamma \tag{A.2}$$

where D_o is a general differential operator, B_o is a boundary operator, $f(r)$ is a known analytical function and Γ is the boundary of the domain Ω. In general, the operator D_o can be divided into a linear part L and a non-linear part N. The eqn.(A.1) can therefore be written as

$$L(u) + N(u) - f(r) = 0 \tag{A.3}$$

By the Homotopy technique, we construct a Homotopy $v(r, p) : \Omega \times [0,1] \to \Re$ that satisfies

$$H(v, p) = (1-p)[L(v) - L(u_0)] + p[D_o(v) - f(r)] = 0 \tag{A.4}$$

$$H(v, p) = L(v) - L(u_0) + pL(u_0) + p[N(v) - f(r)] = 0 \quad \text{A.5)}$$

where $p \in [0, 1]$ is an embedding parameter, and u_0 is an initial approximation of the eqn.(A.1) that satisfies the boundary conditions. From the eqns. (A.4) and (A.5), we have

$$H(v,0) = L(v) - L(u_0) = 0 \tag{A.6}$$

$$H(v,1) = D_o(v) - f(r) = 0 \tag{A.7}$$

When p=0, the eqns.(A.4) and (A.5) become linear equations. When p =1, they become non-linear equations. The process of changing p from zero to unity is that of $L(v) - L(u_0) = 0$ to $D_o(v) - f(r) = 0$. We first use the embedding parameter p as a small parameter and assume that the solutions of the eqns. (A.4) and (A.5) can be written as a power series in p:

$$v = v_0 + pv_1 + p^2 v_2 + \ldots \tag{A.8}$$

Setting $p = 1$ results in the approximate solution of the eqn. (A.1):

$$u = \lim_{p \to 1} v = v_0 + v_1 + v_2 + \ldots \tag{A.9}$$

This is the basic idea of the HPM.

Appendix B:

Solution of the Non-Linear Eqns. (14)-(17) by Using the Homotopy Perturbation Method

Using the Homotopy and new approach to the Homotopy perturbation method to solve the eqn (14) and (15) . In this appendix B, we have indicated how to determine the solution of eqn.(14-15) using the boundary conditions eqs. (16) and (17). In order to solve eqn. (14-15), we construct the Homotopy for the equation as follows:

$$(1-p)\left[\frac{\partial^2 q}{\partial y^2}-\lambda_1 a^* q(y=\infty)-\frac{\partial q}{\partial t}\right]+p\left[\frac{\partial^2 q}{\partial y^2}-\lambda_1 a^* q-\frac{\partial q}{\partial t}\right]=0 \tag{B.1}$$

$$(1-p)\left[\frac{\partial^2 q}{\partial y^2}-\frac{\partial q}{\partial t}\right]+p\left[\frac{\partial^2 q}{\partial y^2}-\lambda_1 a^* q-\frac{\partial q}{\partial t}\right]=0 \tag{B.2}$$

The approximate solution of eqn.(B.2) is

$$q = p^0 q_0 + p^1 q_1 + p^2 q_2 + \ldots\ldots\ldots\ldots \tag{B.3}$$

Subtracting eqn (B.3) into eqn (B.2) and arranging the coefficients of powers of p we get

$$P^0 : \frac{\partial^2 q_0}{\partial y^2}-\frac{\partial q_0}{\partial t}-\lambda_1 \sigma\gamma q_0 = 0 \tag{B.4}$$

$$p^1 : \frac{\partial^2 q_1}{\partial y^2}-\frac{\partial q_1}{\partial t}-\lambda_1 \sigma\gamma q_1-\lambda_1 \sigma\gamma q_0-\lambda_1 a^* q_0 = 0 \tag{B.5}$$

The initial and boundary conditions in eqs.(16)-(17) becomes, at

$$\begin{aligned} &\tau = 0, \quad q_0 = 0 \text{ and } q_i = 0 \ \forall i = 1,2,3\ldots\ldots \text{ and} \\ &\tau = 0 \quad a_0 = \sigma\gamma \text{ and } a_i = 0 \ \forall i = 1,2,3\ldots\ldots \end{aligned} \tag{B.6}$$

$$\begin{aligned} &y = 0,, q_0 = \frac{1}{1+\exp(-\xi)} \ \ q_i = 0 \ \ \forall i = 1,2,3\ldots \\ &y = 0, \frac{\partial a_0}{\partial y} = 0 \text{ and } \frac{\partial a_i}{\partial y} = 0 \ \ \forall i = 1,2,3\ldots\ldots \end{aligned} \tag{B.7}$$

$$\begin{aligned} &y = \infty \quad q_0 = 0, \quad q_i = 0 \ \forall i = 1,2,3\ldots. \\ &y = \infty \quad a_0 = \sigma\gamma, \quad a_i = 0 \ \forall i = 1,2,3\ldots \end{aligned} \tag{B.8}$$

In Laplace plane, eqs (B.7-B.8), become,

$$\begin{aligned} &y = \infty, \quad \overline{q_0} = \frac{1}{s(1+e^{-\xi})} \text{ and} \\ &y = \infty \quad \overline{a_0} = \frac{\sigma\gamma}{s} \end{aligned} \tag{B.9}$$

$$y = 0, \quad \overline{q_0} = 0 \text{ and } \frac{\overline{\partial a_0}}{\partial y} = 0 \tag{B.10}$$

Solving the eqns (B.7) and (B.8) and using the boundary conditions eqns.(B.9) and (B.10),we obtain the following results:

$$\overline{q_0} = \frac{e^{\left(-y\sqrt{s+\lambda_1\sigma\gamma}\right)}}{s(1+e^{-\xi})} \tag{B.11}$$

$$\overline{a_0} = \frac{\sigma\gamma}{s} \tag{B.12}$$

$$\overline{a_1} = \frac{-\lambda_1 \sigma \gamma}{2(1+e^{-\xi})}\left(\frac{e^{-y\sqrt{s}}}{s^2} - \frac{e^{-y\sqrt{s}}}{s\sqrt{s}}\right) \tag{B.13}$$

By taking the Laplace transform for the above eqns. we get the solutions in the text eqns. (18) and (19).

Appendix C: Nomenclature

Symbols	Meaning
T	Temperature
I_P	Height of the catalytic peak
I_p^0	Height of the cathodic peak in the absence of substrate
D	Diffusion coefficient
C_p^0	Concentration of oxidized mediator
C_A^0	Concentration of substrate
F	Faraday constant
R	Resistance
E	Electrode potential
E_{PQ}^0	Standard potential of the mediator couple
a	Mediated concentration of substrate
q	Mediated concentration of substrate
t	Time
X	Distance from the electrode
γ	Excess parameter
σ	Ratio of rate constants
λ_1	rate parameter
τ	Dimensionless time
K_i	rate constants of the homogenous chemical reaction
ψ	Dimensionless current
υ	scan rate of solvent
γ^*	Dimensionless Parameter
ξ	Dimensionless parameter of spherical diffusion
Y	Dimensionless distance
PQ	Redox couple
P	Mediator
A	Substrate
$R_F X$	Substitution of the halogen of perfuroalkyl
X	Halogen
R_F	Perfuroalkyl halides

Dr. V. Ananthaswamy received his M.Sc. Mathematics degree from The Madura College (Autonomous), Madurai-625011, Tamil Nadu, India during the year 2000. He has received his M.Phil degree in Mathematics from Madurai Kamaraj University, Madurai, Tamil Nadu, India during the year 2002. He has received his Ph.D., degree (Under the guidance of Dr. L. Rajendran, Assistant Professor, Department of Mathematics, The Madura College, Tamil Nadu, India) from Madurai Kamaraj University, Madurai, Tamil Nadu, India, during the year October 2013. He has **15** years of teaching experiences in Engineering Colleges, Arts & Science Colleges and Deemed University. He has **3** years of research experiences. At present he is working as Assistant Professor in Mathematics, The Madura College (Autonomous), Madurai-625 011, Tamil Nadu, India from 2008 onwards. He has produced more than **8** M.Phil., Scholars. He has published more than **42** research articles in peer-reviewed National and International Journals and communicated **9** research articles in National and International Journals. Presently he has Reviewer/Editorial Board Member/Advisory Board Member/Editor in **305** reputed National and International Journals. He has reviewed more than **52** research articles in various reputed International Journals related to his research areas. He has completed **one minor research** project sanctioned by UGC in the duration of 18 months. His present research interest includes: Mathematical modeling based on differential equations and asymptotic approximations, Analysis of system of non-linear reaction diffusion equations in physical, chemical and biological sciences, Numerical Analysis, Mathematical Biology, Mathematical and Computational Modeling, Mathematical Modeling for Ecological systems. Also, he has participated 23 and presented 9 research papers in National and International Conferences.

Dr. L. Rajendran received his M.Sc. in Mathematics in 1981 from Presidency College, Chennai, TN, India. He obtained his Ph.D. in Applied Mathematics from Alagappa University, Karaikudi, TN, India during 2000. At present, he is working as a Professor in Matheatics at Sethu Institute of Technology, Madurai, Tamil Nadu, India. Before this position (1986–2007), he was working as a Post Graduate Assistant in Mathematics at SMSV Higher Secondary School, Karaikudi, TN, India. From the year 2008 onwards, he was working as Assistant Professor in the Department of Mathematics, The Madura College (Autonomous), Madurai, Tamil Nadu, India from February 2008 to May 2015. He has 25 years teaching experience and 15 years research experience. He has authored and coauthor over 155 research publications including about 70 scholarly articles in peer-reviewed journals. He has produced more than 20 Ph.D., Scholars in Applied Different Equations. He visited institute fur Organische Chemie, Universitry at Tubingen, D- 72076 Tubingen, Germany in year 2003 under INSA and DFG Postdoctoral Research Fellowship. Currently he has three research projects from DST, CSIR and UGC. His current research interests include mathematical and computational modeling of electrochemical biosensor.